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Distribution of rare earth elements in the Yamuna and the Chambal rivers, India

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We report here the first measurements of dissolved rare earth elements (REE) in the headwaters of the Yamuna river draining through the southern slopes of Himalaya. Due to intense weathering of the surface rocks of different lithologies and influence of tributaries, Yamuna river waters have variable dissolved REE contents ($87 < \sum\text{REE} < 1374$ ng L^{-1}, mean = 288.6 ng L^{-1}) and exhibit negative Eu anomaly ($0.49 < \text{Eu/Eu*} < 0.73$, mean = 0.63). While most of the samples do not show discernable Ce anomalies; a negative Ce anomaly, however, found in a few of them, which can be explained by the colloidal pool preferentially enriched in Ce. A comparison among the river waters and bed sediments suggests that dissolved composition of REE is strongly fractionated and is enriched in MREE (Nd-Gd) with respect to sediments; presumably due to preferential dissolution of phosphate minerals such as apatite during weathering processes.

Along with the Yamuna river, bed sediments from the Chambal river (a Peninsular river) have also been analyzed for REE composition. Bed sediments in the Yamuna and the Chambal river basins are characterized by $\sum$REE concentrations in the range of 78 to 291 μg g^{-1} (mean = 165 μg g^{-1}) and 96 to 157 μg g^{-1} (mean = 134 μg g^{-1}), respectively. A characteristic feature observed in the REE-normalized patterns of bed sediments is a strong HREE enrichment and a relatively positive Eu anomaly with respect to the granites in the Yamuna river catchment. In contrast, the bed sediment samples of the Chambal river show significant LREE enrichment and Eu enrichment with respect to the Deccan basalts in its catchment. The feldspars and their secondary products, which are enriched in Eu, might be the cause of the Eu anomaly. In river sediments of both these basins, the enrichment factors (EF), with respect to PAAS are ≤2 suggesting that REE composition is mainly derived from weathering processes.

Keywords: dissolved rare earth element, MREE enrichment, Yamuna river, Chambal river, bed sediment

INTRODUCTION

Systematic geochemical studies of the large rivers provide information on the sources of various chemical elements to the effluent waters, their fluxes to the oceans, silicate *vis-à-vis* carbonate weathering rates in the basins and associated drawdown of atmospheric CO_2. Many common rock-forming minerals weather at significantly different rates. Thus differential weathering of minerals gives rise to a range of geochemical and isotopic signatures in the weathered sediments. These signatures in suspended and bed sediments remain largely intact when they are ultimately displaced from the catchment areas and transported downstream in a river system. Several studies have attempted to address on a particular aspect of natural river water chemistry such as the role of elevation (Drever and Zobrist, 1992), lithology (Sarin *et al*., 1989, 1992; Pandey *et al*., 1999), climate (Bluth and Kump, 1994), seasonal variations (Devol *et al*., 1995), individual cyclonic discharge events (Alexander *et al*., 2001) or anthropogenic inputs (Douglas *et al*., 2002) in controlling chemical variability and transport of major and trace elements. Likewise, studies on the dissolved load of the Ganga-Brahmaputra river system draining the Himalaya (Sarin and Krishnaswami, 1984; Sarin *et al*., 1989, 1992; Krishnaswami *et al*., 1992; Pande *et al*., 1994; Ahmad *et al*., 1998; Singh *et al*., 1998; Galy and France-Lanord, 1999, 2001; Ramesh *et al*., 2000; Dalai *et al*., 2002; Di-Giovanni *et al*., 2002; Jacobson *et al*., 2002; Stummeyer *et al*., 2002) have contributed significantly to our understanding of the weathering processes that dominate the composition of water and sediments.

The rare earth elements (REE), La-Lu, are widely utilized as tracers of a range of geological processes because of their similar electronic configurations that give rise to predictable differences in chemical behaviour along the series (Henderson, 1984; Elderfield, 1988; Lipin and McKay, 1989). A number of studies have been carried out on the geochemistry of REE in river waters (Keasler and Loveland, 1982; Goldstein and Jacobsen, 1988; Elderfield *et al*., 1990; Sholkovitz *et al*., 1999; Tricca *et al*., 1999; Shiller, 2002) and sediments (Ross *et al*., 1995;

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Rousseau *et al.*, 1996; Singh and Rajamani, 2001). However, studies on the weathering and distribution of REE in the rivers draining the Himalaya and Peninsular India are rather sparse (Ramesh *et al.*, 2000; Singh and Rajamani, 2001). The present study reports on the patterns of REE in sediments and waters from the upstream samples of two river systems, the Yamuna and the Chambal. The Yamuna river, draining the western part of the Ganga catchment along the southern slopes of the Himalaya, is the largest tributary of the Ganga (Negi, 1991). In its course, the Yamuna drains a variety of lithologies in the Lesser Himalaya thereby providing an opportunity to examine the influence of regional geology and lithology on geochemistry of REE. In addition, the strong altitudinal gradients in mountain regions combined with the pristine condition of the area provide unique opportunity to study the geochemical weathering processes. In contrast, the Chambal, a major tributary of Yamuna, drains the Vindhyan and the Indo-Gangetic plain which is undergoing major land-use changes, with large areas of intensely farmed agricultural land, urbanized and industrial regions and open uplands. The Vindhyan is composed of crystalline igneous and metamorphic rocks (Valdiya *et al.*, 1982). This study, for the first time, provides a comparative data on the dissolved REE composition of the Yamuna river along with those in the bed sediments.

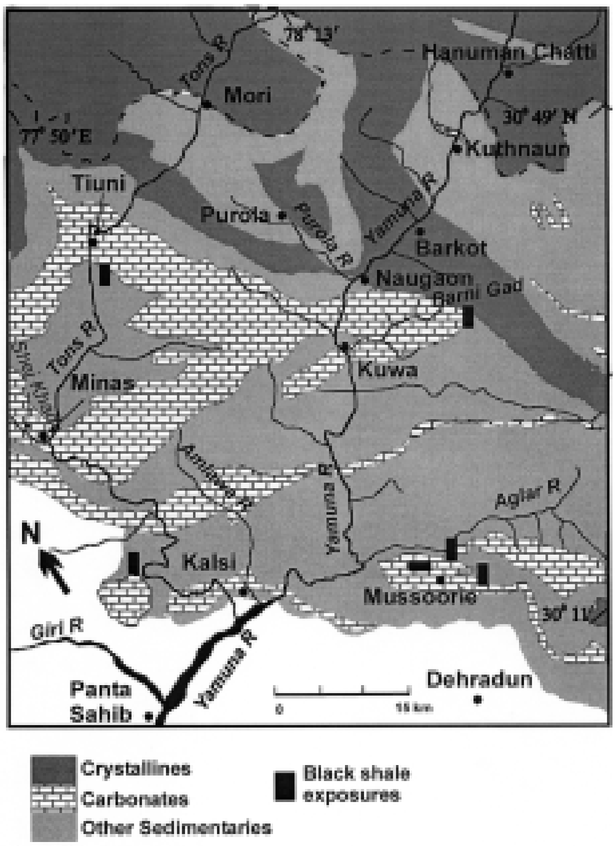

Fig. 1. Simplified, geological lithologies of the Yamuna river catchment in the Himalaya. Only those tributaries that are sampled for REE are shown.

SAMPLES AND GEOLOGIC BACKGROUND

Lithology and hydrology of the Yamuna and the Chambal river catchments

Yamuna river A significant part of the study area for the Yamuna river is contained in the Lesser Himalaya (Fig. 1). The Yamuna originates from the Yamunotri Glacier at the base of the Bandapunch peak in the Higher Himalaya (Negi, 1991; Dalai *et al.*, 2002). The Yamuna has a number of tributaries in the Himalaya, prominent among them are the Tons, Giri, Aglar, Asan and the Bata (Fig. 1). In the lower reaches, the Chambal, Sindh, Betwa, and the Ken are the major tributaries joining the Yamuna from the right bank. The Yamuna flows almost parallel to the Ganga for a distance of ~1380 km before joining it at Allahabad. Among all the tributaries of the Ganga, the Yamuna has the largest drainage area. It receives waters from glacier/snow melt in the source region, from monsoon rains and from springs and various tributaries along its downstream course. Near its source in the Higher Himalaya, the Yamuna drains mainly the crystallines of Ramgarh and Almora groups (Gansser, 1964). Occurrences of calc-schists and marble with sulphide mineralization have been reported in the areas upstream of Hanuman Chatti (Jaireth *et al.*, 1982). From the Higher Himalaya, the Yamuna flows in the southwest direction and enters the Lesser Himalaya where it drains a variety of lithologies. It flows through a large stretch of quartzite of Berinag Formation. Downstream, it passes through the massive dolomitic limestone and marble of Mandhali and Deoban Formations (Fig. 1). The Yamuna then enters a large stretch of the sedimentaries of the Chakrata Formation, Chandpur Formation and Nagthat Formation. Barites occur in the silisiclastic sediments of Nagthat Formations in the Tons river section (Sachan and Sharma, 1993) and in the lower horizons of Krol limestones at Maldeota and Shahashradhara, where they occur as veins (Anantharaman and Bahukhandi, 1984). Southwest of Kalsi, the Yamuna enters the Siwaliks comprising the channel and floodplain deposits by the Himalayan rivers in the past. In the Lesser Himalaya, occurrences of shales are reported into the Infra Krol, the Lower Tal, the Deoban and the Mandhali Formations (Gansser, 1964; Valdiya, 1980). These are exposed at a number of locations in the Yamuna and the Tons catchments, the largest being at Maldeota and Durmala, around Dehradun, where phosphorite is mined economically. Gypsum occurs in Krol Formation in the form of pockets and bands

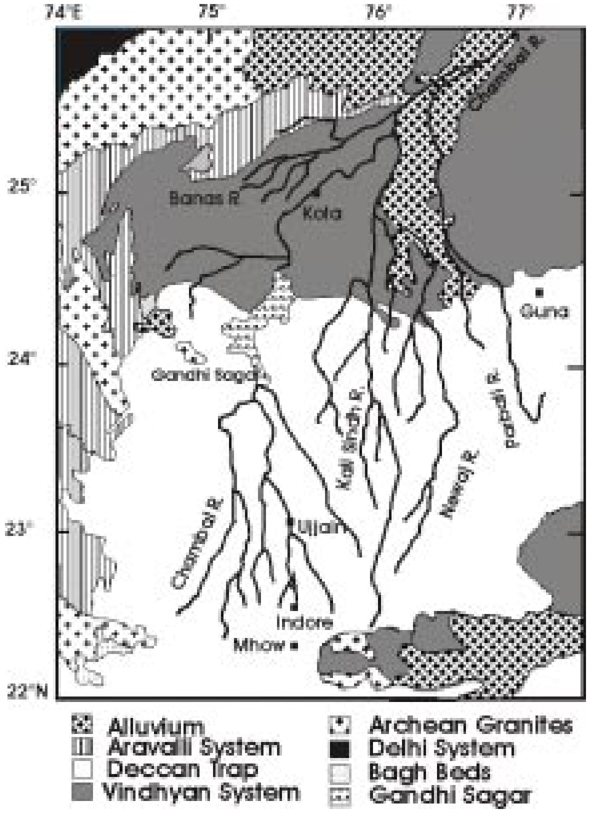

Fig. 2. Simplified, geological lithologies of the Chambal river catchment. Only those tributaries that are sampled for REE are shown.

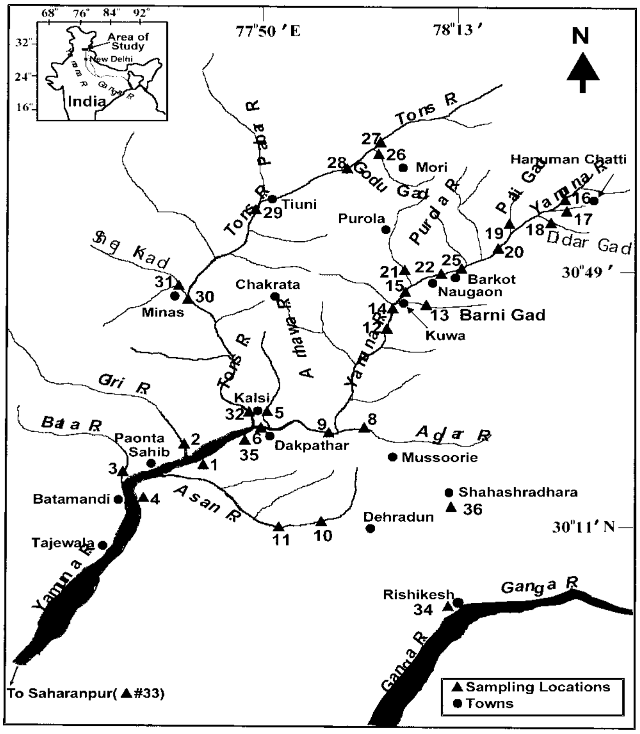

Fig. 3. Sampling locations of the Yamuna river basin. The location numbers given are only for the October 1998 collection. Only those tributaries that are sampled for REE are shown.

(Ananatharaman and Bahukhandi, 1984; Valdiya, 1980). The soils in these regions have been grouped as brown-hill soils (Devi, 1992), which formed from weathering of granite, gneiss and schist. Soils on the slope (15–40%) are shallow due to erosion and mass wasting processes and usually have very thin surface horizons.

The drainage basins of the Yamuna and its tributaries experience tropical monsoon climate with much variability introduced by the altitude, mountain barriers, air masses and their movement (Devi, 1992). The southwest monsoon hits the region around the last week of June and withdraws around the last week of September. The annual rainfall at Dehradun and Kalsi, situated at the foothills of the Himalayas, is ~210 cm whereas in Mussoorie, lying on the windward side of the mountain slope, receives an annual rainfall of ~270 cm. The Yamuna river drains an area of about 9600 km^2 in the Himalaya with an annual water flow of 10.8×10^{12} L at Tajewala (Rao, 1975; Jha *et al.*, 1988). About 80% of water discharge occurs in the month of July to September.

Chambal river The Vindhyan range traverses nearly the whole width of Peninsular India with length of about 1050 km and an average elevation of some 300 meters. Deccan Trap lava flows covers the major areas in the upstream of the Chambal river. Large inliers of old rocks, belonging to the Archaeans, Vindhyan and Gondwanas, out-crop within the Deccan Trap. The Chambal is the principal tributary of the Yamuna and rises in the Vindhyan Range just south of Mhow (Fig. 2), at an elevation of 354 m. The Chambal Basin lies between 22°27′ to 27°N and 73°20′ to 84°E. Vindhyan mountain forms the prominent plateau-like range of sandstones to the north of the Narmada valley, particularly Bundelkhand and Malwa (Krishnan, 1982).

A large part of the soils in the alluvial plains of the Chambal river system (where the annual rainfall is <100 cm) is impregnated with alkaline and saline soils (Sarin *et al.*, 1989). The Chambal catchment exhibits a wide range of land-use types, with large areas of intensely farmed agricultural land, urbanized and industrial regions and open uplands (CBPCWP, 1982). River water is of variable quality, containing effluent from industries and urban conurbations and sediments, nutrients and agrochemicals from the land surfaces.

The climate of the area is warm and humid, with a mean annual minimum and maximum temperatures of

Table 1. Sampling details of bed sediments samples for REE

Sample code	River	Location	Sampling date
Yamuna river and tributaries			
RW98-20	Yamuna	Downstream of Paligad bridge	10/1998
RW98-25	Yamuna	Barkot	10/1998
RW98-22	Yamuna	Upstream of Naugaon	10/1998
RW98-14	Yamuna	Downstream of Barni Gad's confluence	10/1998
RW98-12	Yamuna	Downstream of Nainbaug	10/1998
RW98-9	Yamuna	Downstream of Aglar's confluence	10/1998
RW98-6	Yamuna	Upstream of Ton's confluence	10/1998
RW98-1	Yamuna	Rampur Mandi, Paonta Sahib	10/1998
RW98-4	Yamuna	Downstream of Bata's confluence	10/1998
RW98-33	Yamuna	Yamunanagar, Saharanpur	10/1998
RW98-18	Didar Gad	Hanuman Chatti–Barkot Road	10/1998
RW98-19	Pali Gad	Pali Gad bridge	10/1998
RW98-13	Barni Gad	Kuwa	10/1998
RW98-21	Kamola	Between Naugaon and Pirola	10/1998
RW98-26	Godu Gad	Purola–Mori Road	10/1998
RW98-27	Tons	Mori	10/1998
RW98-29	Tons	Tiuni	10/1998
RW98-31	Shej Khad	Minas	10/1998
RW98-30	Tons	Minas	10/1998
RW98-32	Tons	Kalsi, upstream of confluence	10/1998
RW98-8	Aglar	Upstream of Yamuna bridge	10/1998
RW98-2	Giri	Rampur Mandi	10/1998
RW98-11	Asan	Simla Road bridge	10/1998
Chambal river and tributaries			
CH-1	Chamla	Burnagar	9/1998
CH-2	Chambal	Between Burnagar and Ujjain	9/1998
CH-3	Gambir	Between Burnagar and Ujjain	9/1998
CH-4	Shibra	Ujjain-Agar Road	9/1998
CH-5	Kalisindh	Upstream of barrage on Indore-Guna Road	9/1998
CH-6	Lakunda	Near Chomachoma village	9/1998
CH-7	Chotakalisindh	Bat village	9/1998
CH-8	Newaj	Pachor village	9/1998
CH-9	Dhudhi	Dhudhi village, Tributary of Newaj	9/1998
CH-10	Newaj	Kisanghat village, 5 km before Rajghar	9/1998
CH-11	Charganga	~15 km before Aklera Tributary of Newaj	9/1998
CH-12	Chhapi	Arnia village, Tributary of Kalisindh	9/1998
CH-14	Kalisindh	~20 km to Jhalewar	9/1998
CH-15	Aav	Suket village, Tributary of Kalisindh	9/1998
CH-16	Aamjar	~50 km from Kota, Tributary of Kalisindh	9/1998
CH-17	Kalisindh	Kota-Kisanganj Road	9/1998
CH-18	Parbati	~1 km before Kisankanj	9/1998
CH-19	Tabra	Upstream of bridge on Kota-Bundi Road	9/1998
CH-20	Guda-pachad	Bridge on the Kota-Bundi Road	9/1998
CH-21	Mangli	Bridge on the Kota-Bundi Road	9/1998
Ganga river and tributaries*			
G-1	Yamuna	Saharanpur	11/1983
G-2	Ganga	Rishikesh	11/1983
G-3	Ganga	Gurmukteshwar	11/1983
G-4	Ghaghara	Ayodhya	11/1983
G-5	Yamuna	Allahabad	11/1983
G-6	Ganga	Varanasi	11/1983
G-7	Gomti	Dobni	11/1983

**Sampled during November 1983 (Sarin et al., 1989).*

Table 1. (continued)

Sample code	River	Location	Sampling date
Granites			
GR98-1		Yamuna Bank Hanuman Chatti	10/1998
GR98-2		Yamuna Bank Jharjhar Ghad	10/1998
GR99-1		5 km downstream of Hanuman Chatti	6/1999
GR99-2		5 km downstream of Hanuman Chatti	6/1999

Table 2. Sampling details along with temperature, pH and TDS of water samples for REE

River	Location	Sample code*	Collection date	Temp.** (°C)	pH**	TDS** (mg L^{-1})
Yamuna	Rampur Mandi	RW99-2 (RW98-1)	6/1999	21.9	8.6	194
Giri	Rampur Mandi	RW99-3 (RW98-2)	6/1999	27.8	8.5	547
Ganga	Rishikesh	RW99-6 (RW98-34)	6/1999	15.7	8.4	115
Yamuna	Yamunanagar, Saharanpur	RW99-7 (RW98-33)	6/1999	8.2	8.7	262
Yamuna	Downstream of Barni Gad’s confluence	RW99-11 (RW98-14)	6/1999	21.1	9.1	144
Yamuna	Hanuman Chatti	RW99-13 (RW98-16)	6/1999	10.2	8.7	91
Yamuna	Kuthanur Village	RW99-17 (RW98-21)	6/1999	15.7	8.5	102
Yamuna	Rampur Mandi	RW99-58 (RW98-1)	9/1999	20.6	8.4	109
Ganga	Rishikesh	RW99-59 (RW98-34)	9/1999	18.6	8.4	99
Spring	Shahashradhara	RW99-60 (RW98-36)	9/1999	7.1	7.1	2412
Asan	Simla Road Bridge	RW99-61 (RW98-11)	9/1999	27.4	7.9	461
Tons	Kalsi, upstream of confluence	RW99-63 (RW98-32)	9/1999	21.3	8.5	146
Yamuna	Upstream of Ton’s confluence	RW99-64 (RW98-6)	9/1999	22.1	8.4	140
Yamuna	Downstream of Ton’s confluence	RW99-31	6/1999	26.9	8.4	172
Yamuna	Downstream of Aglar’s confluence	RW99-51 (RW98-9)	9/1999	18.1	8.6	85
Aglar	Upstream of Yamuna Bridge	RW99-52 (RW98-8)	9/1999	22.4	8.5	328
Yamuna	Yamunanagar, Saharanpur	RW99-54 (RW98-33)	9/1999	24.1	8.2	151
Yamuna	Downstream of Bata’s confluence	RW99-55 (RW98-4)	9/1999	27.5	7.7	274
Giri	Rampur Mandi	RW99-57 (RW98-2)	9/1999	26.6	8.3	348
Chambal	Upstream of Jawahar Sagar	CH-22	9/1998	—	8.4	226

—: not measured.

**Sample codes given in parentheses are the corresponding sediment samples collected during non-monsoon period (October 1998, Table 1, Fig. 3).*

***Temperature, pH and TDS data for the Yamuna river samples are from Dalai et al. (2002).*

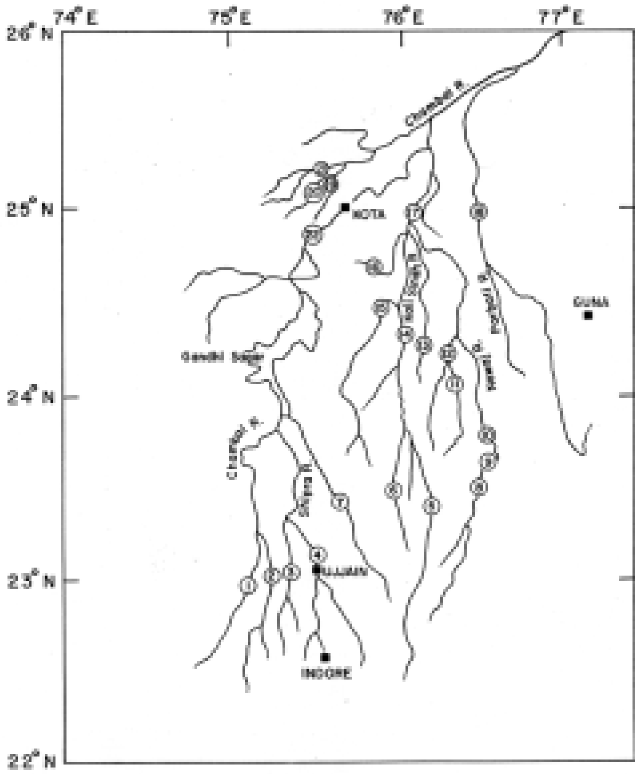

Fig. 4. Sampling locations of the Chambal river basin. Only those tributaries that are sampled for REE are shown. The samples were collected during monsoon season of 1998.

32.2°C and 18.9°C respectively. Temperature displays a bimodal distribution, with peaks in summer (May) and spring (October). The average rainfall is 990 mm in this region, nearly 90% of which is received during the SW monsoon from June to September about 60%, of which is received only for July and August. Length of the Chambal river is 965 km and the area of the catchment is 1.4×10^5 km^2. The mean annual runoff at Udi is 31.4×10^{12} L (Rao, 1975; CBPCWP, 1982).

Sampling of the Chambal and the Yamuna river waters and bed sediments

Water and bed sediment samples from the Yamuna river and its tributaries were collected (Dalai *et al*., 2002) during October 1998 (post-monsoon) from 33 locations (Tables 1 and 2, Fig. 3) and from the Chambal river and its tributaries during September 1998 (post-monsoon) from 22 locations (Table 1, Fig. 4). In addition, water sample was collected from a spring, the Shahashradhara, near Dehradun (Fig. 4). The major ion chemistry of these samples and its implication to silicate-carbonate weathering and atmospheric CO_2 drawdown are discussed elsewhere (Dalai *et al*., 2002; Rengarajan, 2004).

Temperature was measured with a temperature probe (MA Line) with a precision of ±0.1°C. A microprocessor based pH meter (Eutech Cybernetics, Model pH Scan2) was used to measure pH with a precision of ±0.1 unit. Prior to measurements, the meter was calibrated with freshly prepared buffer solutions using buffer Merck® capsules of pH 4, 7, 9.2. For REE, water samples, collected generally from the mid-stream, were filtered through Gelman® 0.4 μm filters and collected in acid-washed polyethylene bottles that were rinsed several times with distilled, deionized water followed by ambient sample water. These were acidified with Ultrex® HNO_3 to give pH of 2. From the same sites, bed sediments were collected from water sample sites that were used for REE analysis of the bulk samples.

ANALYTICAL METHODS

Sediment samples were placed in a hot-air oven at 110°C for 24 hours. After drying, they were crushed to <60 mesh in the agate martar, mixed well to avoid selective crushing and stored in airtight vials until analyzed. REE determination in bulk sediments was accomplished by fusing the sample, dissolving the melt and extracting the REE by using ion exchange chromatography (Cook *et al*., 1986; Govindaraju and Mevelle, 1987; Djingova and Ivanova, 2002). Towards this, 1 g sample was mixed with 2 g lithium metaborate in a platinum crucible and heated to 850°C overnight. The glassy melt was taken in a 150 mL FPA beaker with 100 mL complexing solution (prepared by mixing 50 g of oxalic acid, 500 mL of 14.5N HCl, 25 mL of H_2O_2 and distilled water to make up the volume to 5 L) and stirred on a magnetic stirrer at 80°C for 5 hours. The dissolved solution was directly loaded onto Bio-Rad® AG50-X8 cation exchange resin column (previously conditioned with 1N HCl). Subsequently, the column was washed with 2N HCl (3×30 mL), 10 ml H_2O followed by 15 mL 4N HNO_3. The REE fraction was eluted with 7N HNO_3 (4×30 mL) and the solution was evaporated to almost dryness. The residue was dissolved with 25 mL of 1N HNO_3 and the solution was stored in 30 mL polypropylene bottles for REE assay by the ICP-AES (Jobin Yvon, Model JY38S). The argon plasma was operated with a RF frequency of 40.68 MHz at a forward power of 1200 W. The analytical wavelengths selected are the characteristic lines of the elements, which are free of spectral interference. Except Er, other REE in these standards compared well with the reported values. The precision is expressed as a coefficient of variation [(Std. Deviation/mean)$*$100]. To obtain these data, 6 separate aliquots of the samples/standards were analyzed. The analytical precision (1σ, $n = 6$) in all samples for all REE was better than 5%. Total procedural blanks for the REE in the solution were below 5% (typically <1%) of mea-

Table 3. Range and mean concentrations (ng L^{-1}) of dissolved REE and Eu, Ce and Gd anomalies in the Yamuna river and its tributaries

	Min.	Max.	Geometric mean	Average
La	15.0	267	54.5	77.1
Ce	13.8	558	98.2	156
Pr	2.3	64.9	12.9	18.9
Nd	18.3	253	56.2	77.8
Sm	4.1	60.6	13.6	18.9
Eu	2.0	11.9	4.2	5.0
Gd	4.7	61.0	14.7	20.1
Tb	0.69	8.6	2.2	3.0
Dy	3.0	50.5	12.8	17.3
Ho	0.50	9.2	2.4	3.3
Er	1.3	27.9	6.9	9.2
Tm	0.30	4.2	0.92	1.3
Yb	1.4	21.3	5.4	7.3
Lu	0.50	3.0	1.1	1.4
∑REE	87.0	1374	289	414
∑LREE$^{(1)}$	66.3	1201	239	349
∑HREE$^{(1)}$	11.9	186	46.4	62.4
La_N/Yb_N	3.2	14.7	6.7	7.1
La_N/Sm_N	1.7	7.2	2.5	2.7
Gd_N/Yb_N	1.5	3.3	2.2	2.2
Eu/Eu*$^{(2)}$	0.49	0.73	0.62	0.63
Ce/Ce*$^{(2)}$	0.25	1.2	0.82	0.86
Gd/Gd*$^{(2)}$	0.95	1.3	1.2	1.2

$^{(1)}$LREE are La to Sm and HREE are Gd to Lu.

$^{(2)}$The Eu, Ce and Gd anomalies are calculated as follows:

$Eu/Eu^* = Eu_{CN}/(Sm_{CN} \times Gd_{CN})^{0.5}$.

$Ce/Ce^* = 3Ce_{CN}/(2La_{CN} + Nd_{CN})$.

$Gd/Gd^* = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN})$.

sured values in the solution. In many cases the REE concentrations in the blank solution were below detection limit (5 ng L^{-1}, corresponding to 0.15–0.55 ng g^{-1} in the sediment depending on the volume of the solution after ion exchange column purification). Pure REE standards obtained from Johnson-Matthey were used for analytical calibration. USGS standards, MAG-1, G-2 and W-2 were also run along with samples to monitor the accuracy of the measurements using reported values (Potts *et al.*, 1992).

Dissolved concentrations of REE in river waters were measured at SARM Facility, Centre de Recherches Petrographiques et Geochimiques-CNRS, FRANCE using SCIEX PE ELAN 6000 ICP-MS coupled with on-line liquid chromatography as the sample introduction system. EI CHROM THRU Spec resin was used for REE preconcentration (Carignan *et al.*, 2002). The total extraction yields (close to 100%) is reproducible within 2–5%. Matrix extraction prior to analysis removes possible isobaric interference, eliminates signal suppression in the plasma and makes preconcentration of elements possible.

RESULTS AND DISCUSSION

REE river water chemistry

The ranges and mean values of the dissolved concentration of individual REE and total REE (∑REE) are presented in Table 3. The river water temperature ranged between 7.1 to 27.8°C (Table 2). The pH values of these samples varied from 7.1 to 9.1. In general, pH controls both the absolute abundance of REE in dissolved phase and their relative REE patterns (Sholkovitz, 1995). Higher pH values in river waters result in lower concentrations and more fractionated composition relative to the local rocks in the catchment. Such a trend between pH and ∑REE is observed in the Yamuna river water samples, although the pH range of the measured samples is small.

In river water samples analysed in this study, the contents of REE follow the order: Ce > Nd, La > Pr, Sm, Gd, Dy > Eu, Er, Yb > Tb, Ho, Tm, Lu. ∑REE varied from 87 ng L^{-1} (Giri river at Rampur Mandi, RW98-2) to 1374 ng L^{-1} (Yamuna after the confluence of Bata, RW98-4). REE concentrations vary widely in samples collected in the Yamuna and its tributaries. For example, La concentration ranges from 15 to 267 ng L^{-1}. These values are higher than typical concentration reported for temperate rivers (e.g., the Mississippi river, 10 ng L^{-1} of La, Sholkovitz, 1995). The REE abundance in river waters is controlled by weathering of major and accessory minerals, many of the latter containing high concentrations of REE. Further, the solute-particle interaction in rivers such as ion exchange and absorption on surface coatings also control the REE abundances. In felsic rocks, heavy REE become more leachable with increasing alteration. In basalts with high fractions of glassy components, the leachablility is lower than in basalts with enhanced crystalinity (Möller *et al.*, 2003).

The individual dissolved REE concentrations in the Yamuna river do not show linear relationship between both ∑REE and the TDS (Table 2). This lack of correlation with TDS seems to indicate that the dissolved REE concentrations in these waters are not a simple function of chemical weathering of major lithologies and alkaline, saline soils of the drainage, which dictate TDS content. Likewise, the weak correlation of individual REE with ∑REE reflects their geochemical behaviour in the aqueous phase. The REE are released to river water either disproportionately to the major ions from this basin, a likely inference considering REE are more abundant in resistant accessory phases or that they are sequestered onto various particulate phases after their release. Shale-normalized ratios (shale is Post-Archaean Australian Shale, PAAS, from McLennan, 1989) of light-to-heavy REE (LREE/HREE) in the dissolved phase of the Yamuna river can shed light on the fractionation of these elements during weathering and transport. A ratio of 1 indicates

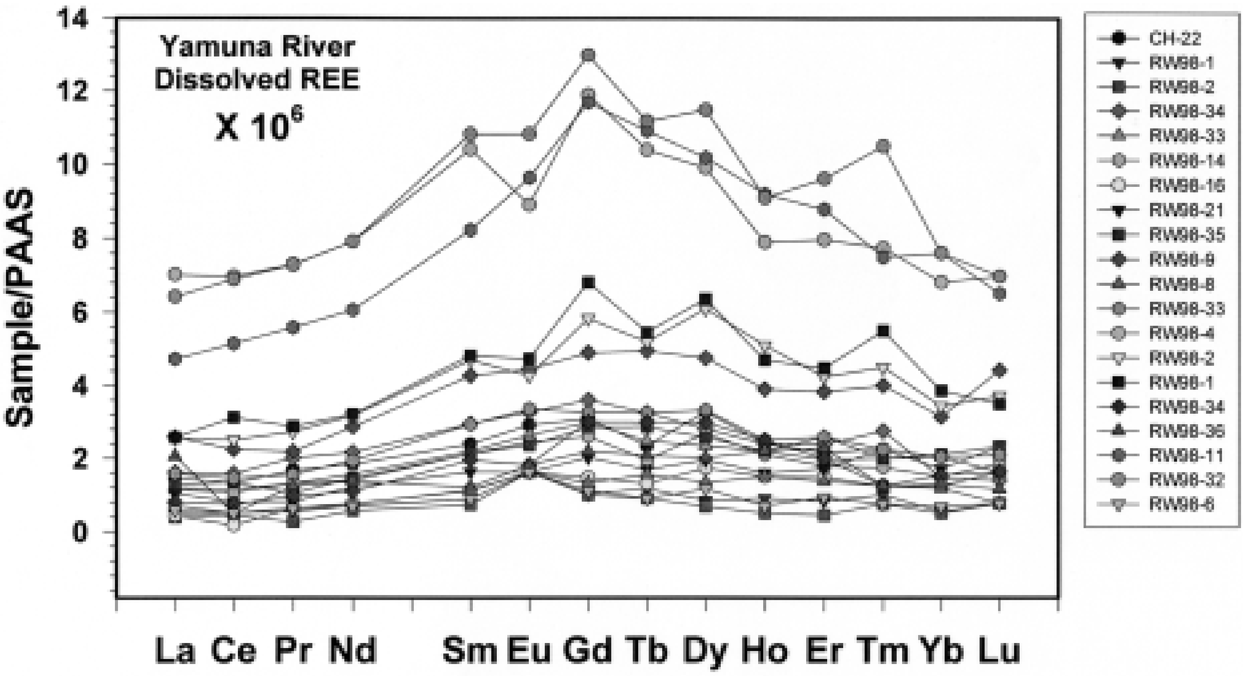

Fig. 5. Dissolved REE concentrations normalized to that of PAAS for the Yamuna river and its tributaries. A large range of REE fractionation is observed among these samples with MREE enrichment.

similar mobilization of these two groups of elements relative to shale. A ratio less than 1 suggests a lower degree of dissolved phase mobilization of the LREE. The shale-normalized ratio of LREE/HREE in the Yamuna river water samples varied from 0.27 to 0.77 with an average value of 0.55.

The shale-normalized patterns of the Yamuna river water samples are plotted in Fig. 5. The slight upward convexity of the REE patterns has also been observed for other river systems such as the Amazon, Fly and Sepik rivers (Goldstein and Jacobsen, 1988; Hannigan and Sholkovitz, 2001). The average REE pattern normalized to PAAS for the river water samples is compared with that of the bed sediments in Fig. 6. It is important to point out here that the REE concentrations in the dissolved phase are 5–6 orders of magnitude lower than those in sediments (Fig. 6). Hence even a very minor release of REE from sediments is adequate to account for their measured concentration in river water. The data in Fig. 6 show middle REE enrichment in the river waters. This enrichment is seen as a hump in the shale-normalized ratios of REE toward the middle of the REE series (MREE, Nd-Gd). Such MREE enrichment is typical of phosphates (Weber *et al*., 1998). The REE pattern in dissolved phase of river waters differ from those in the catchment rocks, a fractionation attributable to geochemical processes influencing their abundances during weathering and/or transport in the streams. These processes enrich dissolved phase in the MREE compared to the LREE and HREE. The behaviour of the REE during weathering of a parent rock is a function of many parameters including (1) the abundance and distribution of mineral phases containing REE in the rocks and sediments of the basin (Aubert *et al*., 2001), (2) the stability of these REE bearing mineral phases with respect to the aqueous fluids involved in the weathering reactions, (3) the chemistry of the aqueous fluids (e.g., pH, eH, concentrations of inorganic and organic complexing ligands (Johannesson *et al*., 1995) and (4) adsorption-desorption reactions of REE with solid surfaces. A comparison of the composition of the Yamuna river water and bed sediments (Fig. 6) suggests that dissolved composition of REE is strongly fractionated and

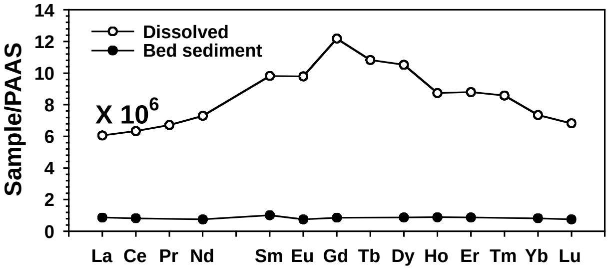

Fig. 6. Distribution of pattern of REE normalized to PAAS in river waters and sediments of the Yamuna river.

Table 4. Inter-element correlation matrix for the dissolved REE of the Yamuna river and its tributaries (n = 20)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1.000	0.981	0.962	0.990	0.945	0.251	0.942	0.224	0.899	0.223	0.688	–0.034	0.562	–0.135
Ce		1.000	0.966	0.995	0.960	0.274	0.961	0.236	0.919	0.228	0.696	–0.031	0.575	–0.125
Pr			1.000	0.975	0.992	0.504	0.984	0.453	0.966	0.444	0.840	0.196	0.740	0.113
Nd				1.000	0.965	0.285	0.965	0.246	0.925	0.243	0.712	–0.018	0.587	–0.119
Sm					1.000	0.538	0.990	0.488	0.982	0.479	0.861	0.233	0.769	0.151
Eu						1.000	0.494	0.986	0.596	0.978	0.915	0.907	0.967	0.895
Gd							1.000	0.451	0.988	0.447	0.849	0.189	0.751	0.098
Tb								1.000	0.547	0.998	0.861	0.952	0.933	0.945
Dy									1.000	0.543	0.898	0.295	0.816	0.217
Ho										1.000	0.846	0.960	0.921	0.958
Er											1.000	0.670	0.982	0.647
Tm												1.000	0.782	0.999
Yb													1.000	0.772
Lu														1.000

is enriched in MREE with respect to sediments. Such trends observed in the Amazon, Fly and Sebik rivers have been attributed by Hannigan and Sholkovitz (2001) to preferential dissolution of more soluble mineral phases such as phosphates (which are enriched in MREE) during weathering processes. Phosphate minerals are enriched in bulk REE concentrations as they substitute for Ca in the apatite lattice (Wright *et al.*, 1987). Apatite, ($Ca_5(PO_4)_3(OH, F, Cl)_2$), is a common accessory phase in metamorphic rocks in a wide range of geological settings and is a relatively common component of the heavy mineral assemblages. Banfield and Eggleton (1989) reported REE mobilization and fractionation resulting from the dissolution of apatite on small scale during weathering of granite. The high Himalayan Crystalline Series is an ~100 m wide belt of leucogranites that extends across the Himalaya (Ayres and Harris, 1997) which contain apatite. While assessing the role of various lithologies in contributing to Sr budget and its isotopic composition of the Yamuna river, Dalai *et al.* (2003) pointed out the significance of minor phases such as calc-silicates, calcites and apatites of the Yamuna basin in contributing dissolved Sr to rivers. Apatites are enriched in Sr, U and REE and weathering of even a small fraction would provide these elements substantially to the dissolved phase.

Inter-element correlation of dissolved REE from the Yamuna river and its tributaries are given in Table 4. A good positive correlation ($r > 0.9$) can be seen between the neighbouring elements except for Ce and Eu. The correlation become worse as two elements are apart to each other in their atomic numbers. Inter-element REE fractionations in the oceans allow insight into basic processes controlling the concentrations and relative abundance of trace elements (Bertram and Elderfield, 1993). Sholkovitz and Szymczak (2000) have shown by studying the Amazon, Fly and Sepik estuarine systems that estuarine reactions can modify the relative abundance of dissolved REE reaching the oceans. They have shown that there are two distinct processes operating on dissolved REE in estuaries, large-scale salt-induced coagulation in the low salinity region and small to extensive release in the mid to high salinity region. Shale-normalized Yb against Nd concentrations of the Yamuna river water samples are plotted in Fig. 7. The river water samples have $(Yb/Nd)_{SN}$ ratio of 1, showing no relative fractionation with respect to shale, whereas that of seawater is 4.3 (Elderfield *et al.*, 1990), indicating an enrichment of HREE over LREE is taking place during estuarine and marine processes.

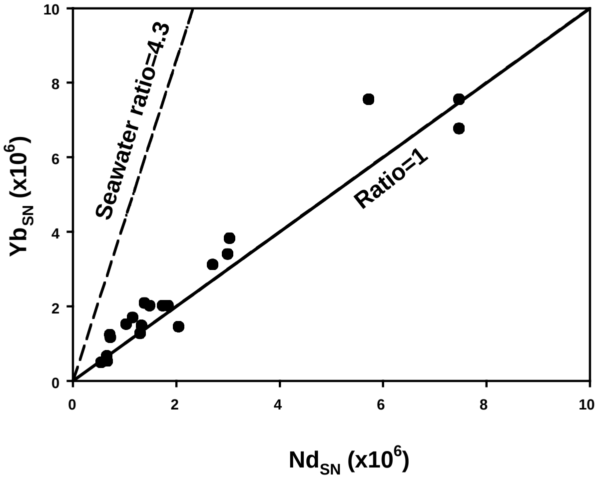

Fig. 7. Scatter plot of PAAS normalized concentrations of Yb vs. Nd of the Yamuna river water samples. Dashed line indicates seawater ratio. The data shows a linear trend with a correlation coefficient, r = 0.9.

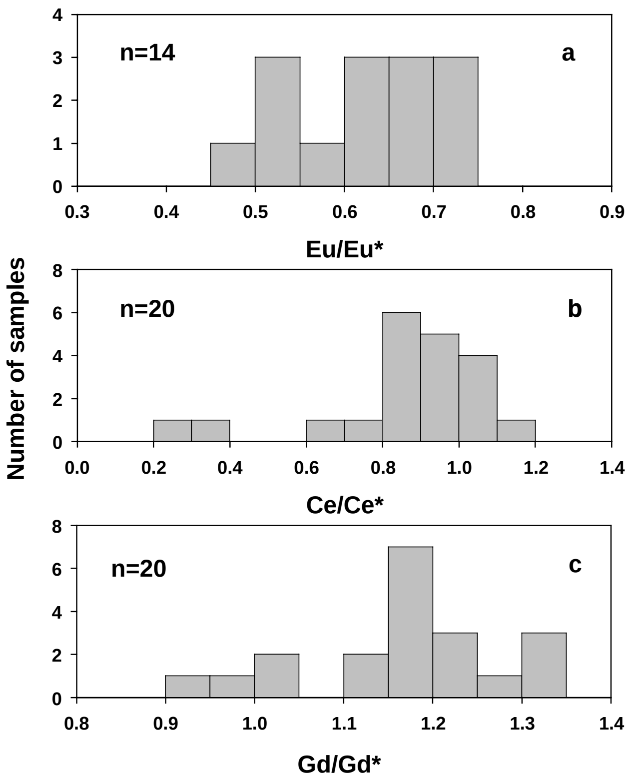

Fig. 8. Histogram of the shale-normalized Eu, Ce and Gd anomalies in the Yamuna river water samples. The samples show negative Eu and negative to slightly positive Ce and Gd anomalies.

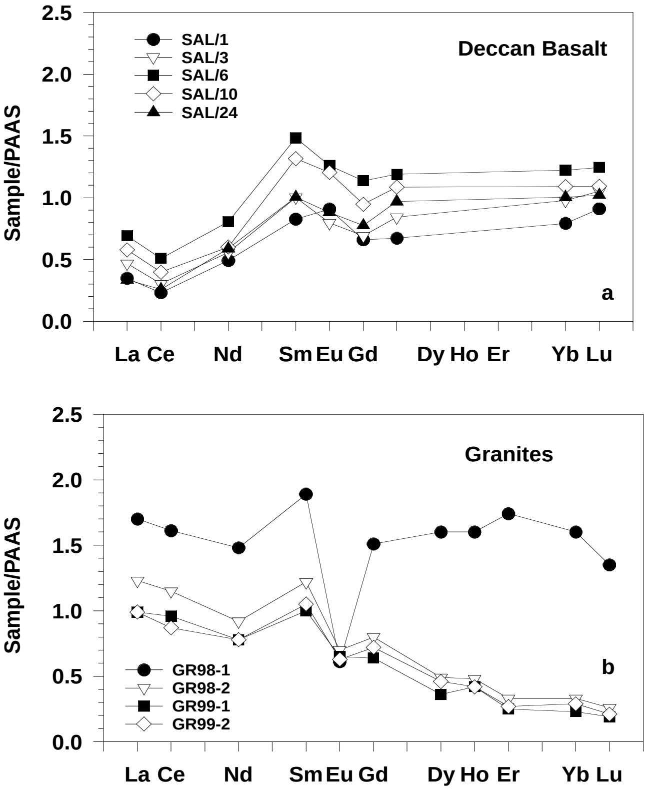

Fig. 9. PAAS normalized REE composition of (a) the Deccan basalts (Sengupta and Deshmukh, 1996) and (b) granite samples from the Yamuna river.

Europium, cerium and gadolinium anomalies in river waters

The Yamuna river water samples show negative Eu anomalies. Chondrite-normalized Eu/Eu* ratios vary between 0.49 and 0.73 (Table 3, Fig. 8). No common sedimentary rock is characterized by Eu enrichment. Similarly river and seawater also show Eu depletion (Martin *et al*., 1976; Elderfield, 1988). Eu depletion in sedimentary rocks and hence the upper continental crust, is due to chemical fractionation within the continental crust, related to production of K-rich granitic rocks, which typically possess negative Eu anomalies (Taylor and McLennan, 1985).

In case of Ce, most of the samples do not show measurable anomalies. However, in a few of them, there is a negative anomaly. Chondrite-normalized Ce/Ce* ratios vary from 0.90 to 1.03 with the exception of six samples (Fig. 8). These samples are from the Yamuna (RW98-16, RW98-21, RW98-9 and RW98-33) and the Aglar (RW98-8) rivers. The Yamuna river at Rampur Mandi (RW98-1) shows the positive Ce anomaly value of 1.16 and the spring sample from Shahashradhara (RW98-36) has the negative Ce anomaly value of 0.25. The samples with negative Ce anomalies also have lower Ce concentrations. The development of negative Ce anomalies in waters is strongly pH dependent and is recognized in mainly alkaline rivers (Elderfield *et al*., 1990; Nelson *et al*., 2003). In the Connecticut River waters by filtering progressively through fine pore size filters (0.45, 0.2 and 0.025 μm), Sholkovitz (1992, 1995) showed that the colloidal pool is preferentially enriched in Ce, leaving the solution phase with a negative Ce anomaly. As mentioned before, these water samples are filtered through 0.4 μm filters and there are no measurements done in the colloidal pool.

Except at the surface, seawater in all oceans shows shale-normalized REE patterns with positive anomalies of La and Gd. These anomalies result primarily from the lower solubility of La and Gd complexes compared to those of their respective neighbours in the REE series. Gd anomaly (Gd/Gd*) in river water (Knappe *et al*., 1999) is quantified by:

$$\mathrm{Gd/Gd^*} = \mathrm{Gd_{SN}}/(0.33\mathrm{Sm_{SN}} + 0.67\mathrm{Tb_{SN}}). \qquad (1)$$

Although the extent of the Gd anomaly in seawater is only small (Gd/Gd* = 1–1.2), it is used as an indicator of the types of ligands that control surface complexation of REE

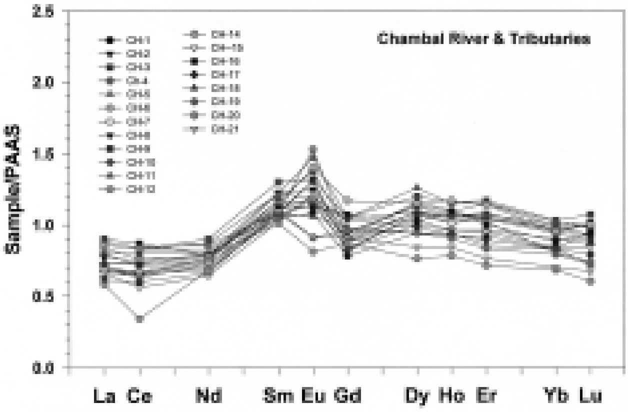

Fig. 10. PAAS normalized REE composition of the bed sediments from the Chambal river and its tributaries.

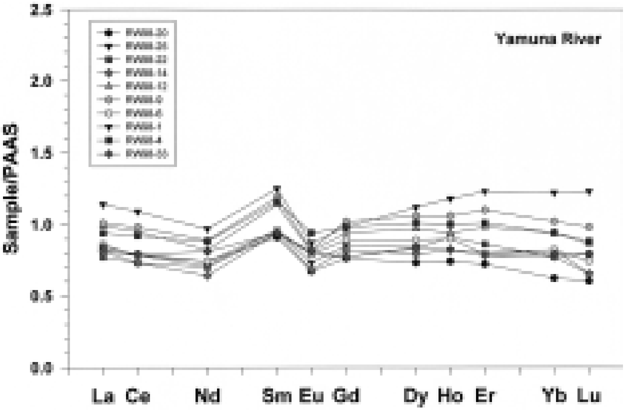

Fig. 11. PAAS normalized REE composition of the bed sediments from the Yamuna river.

on marine particles. Occasionally natural distribution of REE in river waters is modified with anthropogenic influences and show pronounced positive Gd anomalies. This is observed in populated and industrialized regions (Gd/Gd* >2 and up to 1500, closer to the source of contamination, Bau and Dulski, 1996; Nozaki *et al*., 2000; Elbaz-Poulichet *et al*., 2002). The source of the Gd is most likely gadopentetic acid, Gd(DTPA)$^{2-}$, which is used in magnetic resonance imaging (Kummerer and Helmers, 2000). A significant number of the Yamuna river water samples show positive Gd anomalies (shale-normalized Gd/Gd* values 0.95 to 1.32, Fig. 8). These values are less than those reported for rivers in Germany and Japan (Bau and Dulski, 1996; Nozaki *et al*., 2000; Elbaz-Poulichet *et al*., 2002), which have catchments in industrialized areas implying the absence major anthropogenic input of REE to the Yamuna river. This is expected, as all the Yamuna samples are from the upper reaches of the Himalaya.

REE transport in stream sediments

One of the effects of chemical weathering processes is that they distort the chemical composition of the parent rock. For example, granite contains quartz, plagioclase-feldspar and alkali-feldspar. Chemical weathering affects them in the order: plagioclase-feldspar > K-feldspar > quartz. The weathered residues of the feldspars are clay minerals. Thus feldspars progressively gets depleted and the resulting sediments become less representative of the source rock. Thus, the chemistry of bed sediments often does not accurately reflect their source rocks after weathering (Nesbitt *et al*., 1996). However, the abundance and patterns of REE are reasonably well preserved during weathering, as they are far less mobile during sedimentary processes. The normalized REE patterns of the bed sediments from the Yamuna, Chambal and the Ganga rivers and of bedrocks from the Yamuna river catchment are shown in Figs. 9–11. For comparison, a few samples available from the Ganga river along the plains (Sarin *et al*., 1989) were also analyzed for REE composition and the results are also shown in Fig. 12. Data normalization was done with PAAS REE concentrations (Taylor and McLennan, 1985).

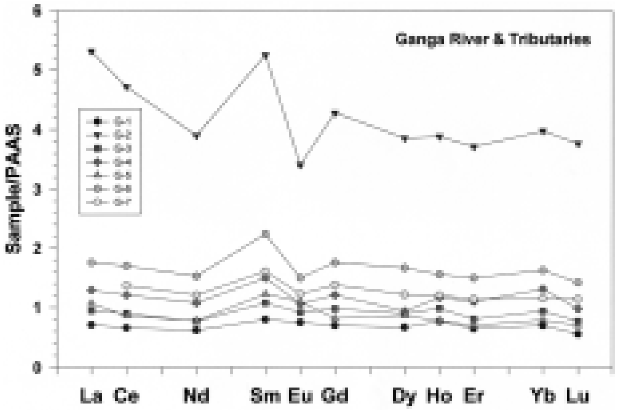

Fig. 12. PAAS normalized REE composition of the bed sediments from the Ganga river and its tributaries sampled during March 1982 and November 1983 (Sarin et al., 1989).

In the Yamuna and the Chambal river basins, due to their dissected topography and the small size, intense mixing phenomena are not favoured and the fast-flowing streams inhibit the weathering reactions. These physicochemical conditions and mildly alkaline pH values of the river water have an important influence on the REE patterns of the sediments of these rivers. A conspicuous characteristic in the REE-normalized pattern of the Yamuna bed sediments is the strong HREE enrichment with respect to granites at Hanuman Chatti, source rocks for the

Table 5. Range and mean concentrations of REE in the Yamuna and the Chambal river bed sediments

	La	Ce	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu	ΣREE	ΣLREE	ΣHREE
								(μg g^{-1})						
Yamuna main stream (n = 10)														
Min.	29.5	57.7	21.9	5.0	0.72	3.6	3.4	0.73	2.1	1.8	0.26	129.4	115.7	11.8
Max.	43.7	86.6	32.9	6.9	1.01	4.7	5.2	1.17	3.5	3.5	0.53	189.5	170.1	18.5
Geometric mean	34.0	67.3	26.6	5.7	0.85	4.1	4.2	0.90	2.5	2.4	0.34	149.1	133.7	14.5
Average	34.3	67.9	26.8	5.8	0.85	4.1	4.3	0.91	2.6	2.5	0.35	150.3	134.8	14.6
Yamuna tributaries (n = 13)														
Min.	17.8	33.0	14.8	3.3	0.58	2.1	2.6	0.51	1.6	1.4	0.20	77.9	68.8	8.5
Max.	67.7	134.5	52.9	11.3	1.25	7.7	8.1	1.88	6.0	6.2	0.94	291.4	262.5	28.4
Geometric mean	37.4	74.8	29.6	6.4	0.96	4.5	4.9	1.05	3.1	3.0	0.43	166.4	148.3	16.9
Average	39.6	79.6	31.2	6.8	0.99	4.8	5.2	1.13	3.3	3.2	0.48	176.3	157.2	18.1
Chambal river (n = 20)														
Min.	22.2	27.0	21.5	5.6	0.88	3.6	3.6	0.77	2.0	1.9	0.26	95.9	78.0	12.6
Max.	34.4	69.5	30.5	7.2	1.65	5.5	5.9	1.16	3.3	2.9	0.46	156.7	136.9	18.5
Geometric mean	28.4	55.2	25.7	6.2	1.28	4.4	4.9	1.00	2.8	2.5	0.37	133.3	115.8	16.0
Average	28.6	56.2	25.8	6.2	1.29	4.4	4.9	1.00	2.8	2.5	0.38	134.2	116.8	16.0
Ganga river* (n = 7)														
Min.	27.2	52.6	21.0	4.5	0.81	3.3	3.1	0.76	1.9	2.0	0.24	117.4	105.3	11.2
Max.	203	375.1	132.3	29.2	3.7	20.0	18.1	3.9	10.6	11.2	1.6	808.5	739.5	65.3
Geometric mean	54.9	104.6	39.6	9.0	1.4	6.2	5.7	1.3	3.3	3.6	0.47	230.0	208.2	20.4
Average	68.5	129.8	48.0	10.9	1.5	7.4	6.8	1.5	3.9	4.2	0.57	283.0	257.1	24.4
All bed sediments (n = 50)														
Min.	17.8	27.0	14.8	3.3	0.58	2.1	2.6	0.51	1.6	1.4	0.20	77.9	68.8	8.5
Max.	203.0	375.1	132.3	29.2	3.7	20.0	18.1	3.9	10.6	11.2	1.6	808.5	739.5	65.3
Geometric mean	34.7	68.0	28.5	6.5	1.1	4.6	4.8	1.0	2.9	2.7	0.39	155.9	138.0	16.5
Average	38.2	74.9	30.5	6.9	1.2	4.9	5.1	1.1	3.1	2.9	0.43	169.2	150.6	17.5
Granites (n = 4)														
Min.	37.7	69.3	26.3	5.6	0.66	3.0	1.7	0.42	0.72	0.65	0.08	147.5	139.2	6.5
Max.	65.0	127.9	50.1	10.5	0.76	7.1	7.5	1.6	5.0	4.5	0.58	280.2	253.4	26.2
Geometric mean	45.7	88.8	32.4	6.9	0.70	4.0	2.8	0.60	1.28	1.2	0.15	185.4	173.8	10.3
Average	46.9	91.3	33.6	7.2	0.70	4.3	3.4	0.73	1.85	1.7	0.22	191.9	178.9	12.2

**Sampled during November 1983 (Sarin et al., 1989).*

Yamuna river sediments. The shale-normalized REE patterns of the Chambal river sediments are similar to Deccan basalts, the primary sediment source of the Chambal river.

Bed sediments in the Yamuna and the Chambal river basins are characterized by ΣREE concentrations in the range of 78 to 291 μg g^{-1} (mean = 165 μg g^{-1}) and 96 to 157 μg g^{-1} (mean = 134 μg g^{-1}), respectively (Table 5). ΣREE concentrations of the Yamuna river sediments by and large fall in the range of that in the source rock (granite) in Hanuman Chatti (Table 5). In the Chambal river sediments, ΣREE are marginally lower than that of the Yamuna sediments and are similar to that in the Deccan basalts (Mahoney *et al.*, 2000). In sediments, the contents of REE follow the order: Ce > La > Nd > Sm > Eu, Yb, Tb, Lu. The average values of LREE and HREE in bed sediments of both rivers are 151 and 17.5 μg g^{-1} respectively (Table 5). Ratios of LREE/HREE in sediments vary from 7.2 to 11.8 in the Yamuna (geometric mean = 9.0) and from 4.8 to 9.9 in the Chambal (geometric mean = 7.3) respectively. The parent granite rocks at Hanuman Chatti in the Yamuna catchment have LREE/HREE in the range from 9.7 to 22.4 with a mean of 16.9. The relatively low LREE/HREE ratios in the Yamuna river sediments reveal that HREE are enriched in the suspended particulate matter of the river water with respect to the parent rock, *viz.* granites. The variation in REE content of sediments from different locations is very small. Comparing the results of this study with data from the Yangtze river system, the lower reaches of the Yellow river (Zhang *et al.*, 1998), world average (Bowen, 1979; Martin and Meybeck, 1979) and PAAS (Taylor and McLennan, 1985), it is observed that these data overlap considerably (Table 6). As discussed in the previous section, ratios of LREE/HREE for the Yamuna water samples vary from 2.6 to 7.3. This difference can be explained by the MREE enrichment in the dissolved phase relative

Table 6. Comparison of REE contents in sediments and source rocks for various rivers ($\mu g\ g^{-1}$)

River*	La	Ce	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu
(1)	34.3	67.9	26.8	5.8	0.85	4.1	4.3	0.91	2.6	2.5	0.35
(2)	28.6	56.2	25.8	6.2	1.3	4.4	4.9	1.0	2.8	2.5	0.38
(3)	46.9	91.3	33.6	7.2	0.70	4.3	3.4	0.73	1.9	1.7	0.22
(4)	18.5	27	20.6	6.25	1.09	3.9	—	—	—	2.9	0.46
(5)	16.7	35.9	22.2	5.2	1.68	5.9	5.05	1.01	2.46	2.2	0.32
(6)	47	91	42	6.4	1.07	—	—	—	—	2.3	0.39
(7)	45	88	43	6.2	1.38	—	—	—	—	2.5	0.40
(8)	51	103	47.4	9.1	1.9	—	0.98	—	—	3.7	—
(9)	33.8	73.6	35.4	6.4	1.2	—	—	—	—	2.8	0.45
(10)	41	83	32	6.4	1.2	—	—	—	—	3.6	0.70
(11)	45	95	35	7	1.5	5	—	1	3	3.5	0.5
(12)	38.2	79.6	33.9	5.55	1.08	4.66	4.68	0.99	2.85	2.82	0.43
(13)	30	64	26	4.5	0.88	3.8	3.5	0.80	2.3	2.2	0.32

**(1): Average concentration of sediments from mainstream of the Yamuna river (present study).*
(2): Average concentration of sediments from mainstream of the Chambal river (present study).
(3): Granites from the Yamuna catchment near Hanuman Chatti (this study).
(4): Basalts from the Chambal catchment (Sengupta and Deshmukh, 1996).
(5): Deccan Basalts from Toranmal (21°53′ N, 74°28′ E) (Mahoney et al., 2000).
(6): Sediments in mainstream of the Yangtze river (Zhang et al., 1998).
(7): Suspended matter in mainstream of the Yangtze river (Zhang et al., 1998).
(8): Sediments in the Amazon river (Gaillardet et al., 1997).
(9): Sediments from lower reaches of the Yellow river (Zhang et al., 1998).
(10): Sediments, world average (Bowen, 1979).
(11): Suspended matter, world average (Martin and Meybeck, 1979).
(12): Post Archean average Australian Shale (Taylor and McLennan, 1985).
(13): Continental upper crust (Taylor and McLennan, 1985).

to the bed sediments due to apatite weathering.

Chondrite-normalized (La/Yb) ratios of the Yamuna and the Chambal bed sediments range between 5.7 and 13.7 with a mean of 8.8. The Deccan Basalts have chondrite-normalized (La/Yb) ratio of 5.2, which is lower than that of the granites from Hanuman Chatti (28.7) and PAAS (9.2). The sediments of the Chambal river, derived from the Deccan basalts, have lower $(La/Yb)_{CN}$ ratios compared to that of the Yamuna river. The Chambal sediment samples have $(La/Yb)_{CN}$ ratios from 5.9 to 8.8. Samples CH-19, CH-20 and CH-21 have slightly higher $(La/Yb)_{CN}$ ratios as these samples are derived from the Vindhyan rocks. In general, the Yamuna mainstream samples have $(La/Yb)_{CN}$ ratios from 8.6 to 9.6 except for the uppermost sample of the Yamuna (RW98-20), which has a ratio of 11.8. The bed sediments of the tributaries of the Yamuna river have a range of $(La/Yb)_{CN}$ ratios from 5.7 to 13.7. PAAS normalized (La/Yb) ratios of the corresponding samples vary between 0.6 and 1.5 with a mean of 1.0, lower than the values reported in literature as world average values for suspended load material (1.6–2.7, Goldstein and Jacobsen, 1988).

Distribution of Eu and Ce anomalies of the sediments from the Yamuna and the Chambal river catchments are shown in Fig. 13. It is likely that the variation in the Ce/Ce* anomaly reflects the process of preferential scavenging of Ce by Fe oxyhydroxides which is a common process during transport (Braun *et al*., 1990). The presence of Fe-Mn oxyhydroxides as coatings on suspended and bed sediments and their ability to scavenge trace metals, particularly REE, in freshwater environments is well known (Sholkovitz, 1995; Douglas *et al*., 1999). In general, Ce/Ce* anomaly ranged between 0.83–1.03 for the bed sediments in these river systems (Fig. 13). These values are similar to that observed in the source rocks, namely granites at Hanuman Chatti and average Deccan Trap basalts. Ce is not linearly increasing with Mn and Fe in the bed sediment samples. Complexation of REE to Fe-Mn oxyhydroxides has only minor influence on overall REE geochemistry of bed sediments. However, one sample, CH-12, which is having 44.8% $CaCO_3$, has Ce/Ce* ratio of 0.55. This may be due to mixing of detrital clay and marine limestone present in that sample location.

Eu anomaly values do not vary significantly in the Yamuna river sediments (Fig. 13). Average upper crust as well as granites have a Eu/Eu* value of 0.65. Any Eu^{2+} released during weathering will be oxidized to Eu^{3+}, and hence behave like the other trivalent REE. The presence of Eu anomaly is thus the signature of earlier events in a more reducing igneous environment than that existing at

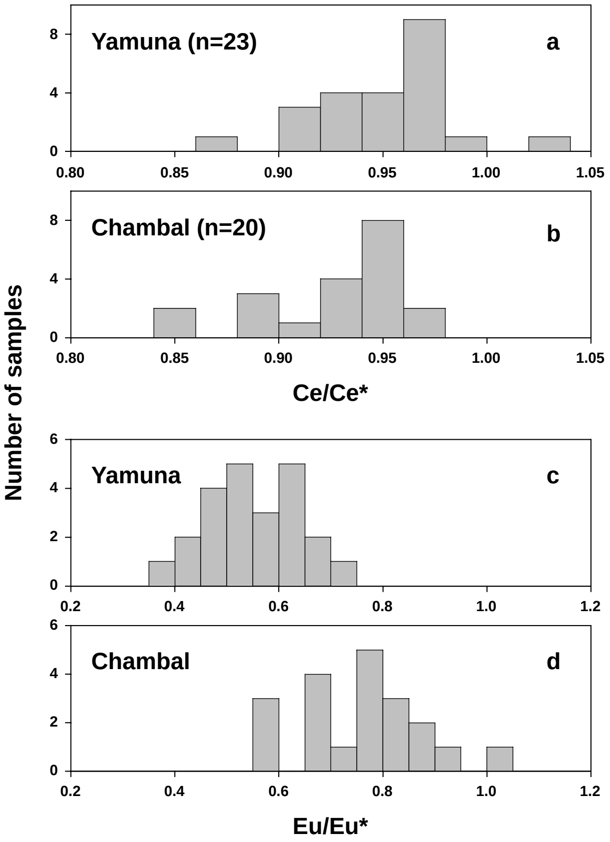

Fig. 13. Distribution of Ce and Eu anomalies in bed sediments of the Yamuna and the Chambal rivers.

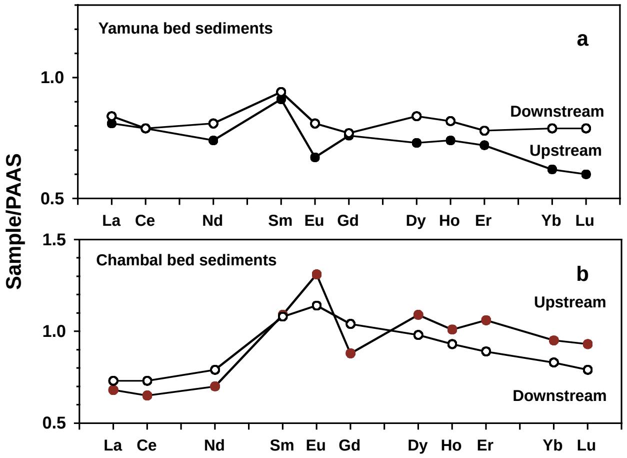

Fig. 14. Distribution pattern of REE normalized to PAAS of the upstream and downstream samples from the Yamuna and the Chambal rivers. a: HREE are enriched relative to LREE in the downstream bed sediments of the Yamuna river, $(La/Lu)_{upstream}/(La/Lu)_{downstream}$ = 1.3. b: In case of the Kali Sindh, a tributary of the Chambal river, HREE are depleted in the downstream sediments, $(La/Lu)_{upstream}/(La/Lu)_{downstream}$ = 0.8.

present in the upper crust. This is contrary to the Chambal river sediments, which show significant LREE and Eu enrichment with respect to the Deccan Trap basalts. The feldspars and their secondary products, which are both enriched in Eu, might be the cause of the changes in Eu anomaly values. There are minor variations in Eu/Eu* ratios in the bed sediments, implying the contribution of tributaries joining the main stream and also due to changes in the lithology during the erosion processes (Fig. 13, Allègre *et al*., 1996).

Assuming the Eu anomaly values are specific to the tributaries one can calculate the contribution of bed sediments by knowing the Eu anomaly values of the main river before and after the confluence of the tributary. The fraction of sediments coming from the tributary, f, is calculated as:

$$fx + (1 - f)y = z \quad \text{and} \quad f = (z - y)/(x - y) \qquad (2)$$

where x, y and z are the Eu anomaly values of the sediment samples from the tributary, and of the main stream before and after the mixing. In the case of the Purola river joining the main Yamuna river, the fraction of sediments coming to the main stream is ~10%. On the other hand, Godu Gad mixing with the Tons river, the calculated fraction of the sediments to the main stream is ~67%.

The normalized REE patterns for total concentrations of the bed sediment samples both at the upstream and downstream locations of the Yamuna and the Chambal rivers are shown in Fig. 14. It is evident that the LREE are enriched with respect to the HREE in the downstream samples $[La/Lu]_{20}/[La/Lu]_{33}$ = 1.26, the numbers 20 and 33 denote samples from the upstream (RS98-20) and downstream (RS98-33) of the Yamuna river, respectively. In the case of the Chambal river, the LREE are depleted with respect to the HREE along downstream: $[La/Lu]_5/[La/Lu]_{17}$ = 0.8, the numbers 5 and 17 denote samples from the upstream (CH-5) and downstream (CH-17) of the Kali Sindh, a tributary of the Chambal river, respectively. Sedimentary transport may also result in changing REE patterns due to heavy mineral (notably zircon and monazite) fractionation (McLennan, 1989) and most likely to be a significant influence in clastic sediments such as quartzites with low REE abundances.

Enrichment factor for trace and rare earth elements

La, Ce and Nd along with trace element composition of the bed sediments in the Yamuna and the Chambal rivers and their several tributaries are plotted in Fig. 15 after normalizing to upper continental crust (UCC) values (Taylor and McLennan, 1985). The major and trace element data are from Dalai *et al*. (2004) and that of the Chambal river are from Rengarajan (2004). Such a repre-

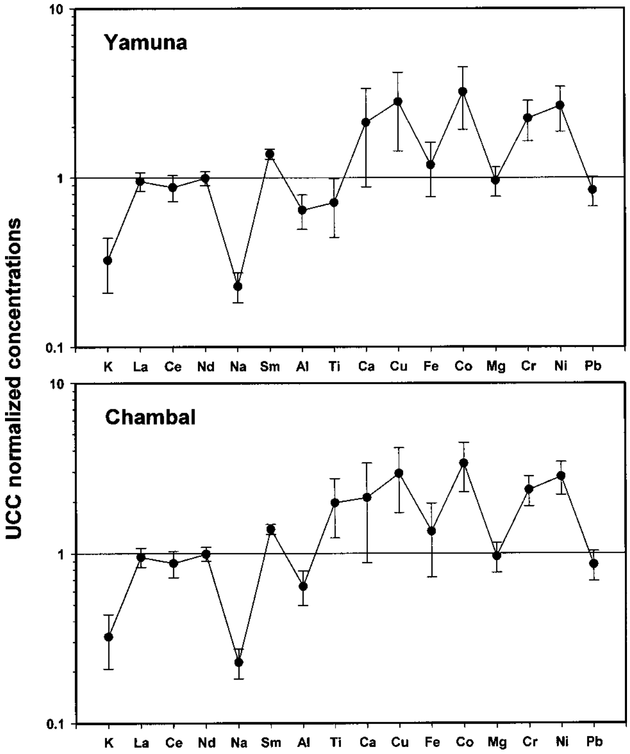

Fig. 15. UCC-normalized multi-elemental diagram of the bed sediment samples from the Yamuna and the Chambal rivers. Major ion data for the Yamuna river sediments are from Dalai et al. (2004) and for the Chambal river from Rengarajan (2004).

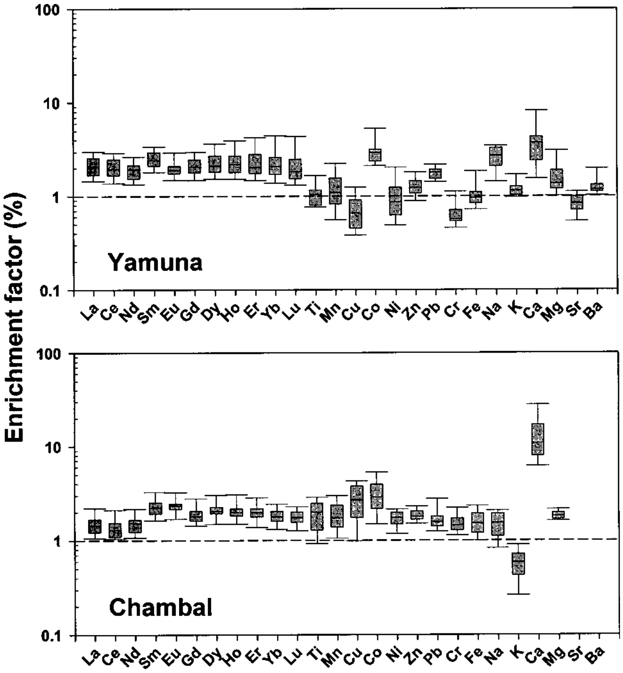

Fig. 16. The variations of the enrichment factor with respect to PAAS of the different elements in bed sediment samples from the Yamuna (n = 23) and the Chambal (n = 20) rivers are shown box plot representing statistical values. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median and the boundary of the farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles. Note the trace elements in the Yamuna river show a decrease in concentrations due to quartz dilution and association with various geochemical phases in sediments.

sentation has previously been used for the Congo basin by Rousseau *et al.* (1996) and for the Amazon basin by Gaillardet *et al.* (1997). The UCC-normalized elemental plot exhibit ample variability with enriched Ca. Adsorption may explain the enrichment with respect to UCC concentrations of metals like Ni, Cr, Co and Cu, whose enhanced concentrations are mostly the result of anthropogenic inputs. Fe, Mg and to some extent Ti are basically unaffected and have concentrations similar to the UCC and those that are less fractionated during weathering and transport (e.g., the REE).

In order to estimate the contribution of elements to sediments from other than natural sources, enrichment factors (EF) with respect to the composition of PAAS (Taylor and McLennan, 1985) are calculated.

$$\mathrm{EF} = (X/\mathrm{Al})_{\mathrm{sample}}/(X/\mathrm{Al})_{\mathrm{PAAS}} \qquad (3)$$

where $(X/\mathrm{Al})_{\mathrm{sample}}$ denotes the measured element/aluminum ratio of the sample and $(X/\mathrm{Al})_{\mathrm{PAAS}}$ denotes the corresponding element/aluminum ratio in PAAS. Distribution of EF for the REE along with trace elements is shown in Fig. 16. A value of EF ≤ 2 can be considered to be of natural origin and a value of >2 is suggestive of anthropogenic sources (Grousset *et al.*, 1995). In both the Yamuna and the Chambal river sediment samples, all heavy metals, except cobalt, have EF ≤ 2 suggesting that they are mainly of natural origin. K remained moderately depleted in the Chambal river samples probably due to the relatively low K-rich igneous rocks in the Deccan Traps.

The proportion of enrichment of REE of the bed sediments remained similar with increasing atomic number. HREE are more soluble and more strongly complexed than middle or light REE and the LREE are more strongly absorbed on most subtracts (Byrne and Kim, 1990). Another factor that might explain the LREE enriched pattern, which was also pointed out by Goldstein and Jacobsen (1988) is mechanical sorting of the stream water suspended material. The HREE are concentrated in many heavy minerals, e.g., zircon and garnet. Since these minerals are preferentially transported along the streambed they may not have been sampled.

CONCLUSIONS

The Yamuna and the Chambal watersheds were studied for the geochemistry of REE. The Yamuna river waters have variable dissolved REE contents ($87 < \sum\text{REE} < 1374$ ng L^{-1}, mean = 288.6 ng L^{-1}) and displays negative Eu anomaly ($0.49 < \text{Eu/Eu*} < 0.73$, mean = 0.63). In case of Ce, most of the samples do not show discernable anomalies. However, in a few of them, there is a negative anomaly. These samples are from the Yamuna (RW98-16, RW98-21, RW98-9 and RW98-33) and the Aglar (RW98-8) rivers. One sample collected from the Yamuna river at Rampur Mandi (RW98-1) shows the highest Ce anomaly value of 1.16 and the spring sample from Shahashradhara (RW98-36) has the lowest value of 0.25. The samples with negative Ce anomalies are also having lower Ce concentrations. These deviations can be explained by the colloidal pool, which is preferentially enriched in Ce, leaving the solution phase with a negative Ce anomaly. A comparison of river water composition and bed sediments suggests that dissolved composition of REE is strongly fractionated and is enriched in MREE (Nd-Gd) with respect to sediments, presumably due to preferential dissolution of phosphate minerals during weathering processes while the sediment pattern of REE is nearly flat. The preferential dissolution of phosphatic minerals such as apatite during weathering can result in extensive REE fractionation between bulk river sediment and water, leading to freshwaters with MREE enrichments.

Bed sediments in the Yamuna and the Chambal river basins are characterized by $\sum$REE concentrations in the range of 78 to 291 μg g^{-1} (mean = 165 μg g^{-1}) and 96 to 157 μg g^{-1} (mean = 134 μg g^{-1}), respectively. The average values of LREE and HREE in bed sediments of both rivers are 150.6 and 17.5 μg g^{-1} respectively. Ratios of LREE/HREE in sediments vary from 7.20 to 11.77 with a geometric mean value of 8.95 and from 4.81 to 9.92 with a geometric mean value of 7.26 in the Yamuna and the Chambal rivers respectively. The Chambal river sediments are having shale-normalized REE pattern similar to Basalt due to the primary weathering of the Deccan basalts. Whereas the Yamuna river sediments are having shale like REE pattern due to the weathering of secondary metamorphosed rocks. The most remarkable characteristics observed in the REE-normalized patterns of bed sediments are a strong HREE enrichment and a relatively positive Eu anomaly with respect to the granites at Hanuman Chatti at the Yamuna river catchment. Where as the samples of the Chambal river show significant LREE enrichment and Eu enrichment with respect to the Deccan basalts at its catchment. The feldspars and their secondary products, which are both enriched in Eu, might be the cause of the Eu anomaly. Significant variations of Ce/Ce* are not observed for the bed sediments in these river systems. HREE are enriched relative to LREE in the downstream bed sediments of the Yamuna river, $(\text{La/Lu})_{\text{upstream}}/(\text{La/Lu})_{\text{downstream}} = 1.3$. In case of the Kali Sindh, a tributary of the Chambal river, HREE are depleted in the downstream sediments, $(\text{La/Lu})_{\text{upstream}}/(\text{La/Lu})_{\text{downstream}} = 0.8$.

Chemical weathering reactions on the continents lead to extensive fractionation between the dissolved REE composition of river waters and that of river sediments and continental rocks. Solution and surface chemistry play a major role in establishing the REE composition of freshwater. Such detailed study on the distribution of REE in rivers helps to elucidate the pattern of their supply to the oceans *via* rivers.

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